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## PROVISIONAL APPLICATION COVER SHEET

for filing a PROVISIONAL APPLICATION under 35 CFR 1.53 (c).

US PTO  
JC872 U.S. PTO  
60465685

		Docket Number	62260	Type a plus sign (+) inside this box
INVENTOR(s)/APPLICANT(s)				
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** <input checked="" type="checkbox"/> Additional inventors are being named on separately numbered sheets attached hereto**				
TITLE OF THE INVENTION (280 characters max)				
IMPROVED PROCESS TO MAKE VEGETABLE OIL BASED POLYOLS AND POLYOLS MADE THEREFROM				
CORRESPONDENCE ADDRESS				
THE DOW CHEMICAL COMPANY Intellectual Property P. O. Box 1967 Midland, MI 48641-1967 U.S.A.	Telephone: 989-636-2540  Fax: 989-636-3237			
ENCLOSED APPLICATION PARTS (check all that apply)				
<input checked="" type="checkbox"/> Specification	Number of Pages	70	<input type="checkbox"/> Small Entity Statement	
<input type="checkbox"/> Drawing(s)	Number of Sheets		<input type="checkbox"/> Other (specify)	
METHOD OF PAYMENT (check one)				
<input type="checkbox"/> A check or money order is enclosed to cover the Provisional filing fees			PROVISIONAL FILING FEE AMOUNT	\$160.00
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees and credit Deposit Account Number:	04-1512			
The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government				
<input checked="" type="checkbox"/> No <input type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are:				

Respectfully submitted,

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## PROVISIONAL APPLICATION FILING ONLY

## PROVISIONAL APPLICATION COVER SHEET

Page 2

			Docket Number	62260
<b>TITLE OF THE INVENTION (280 characters max)</b>				
IMPROVED PROCESS TO MAKE VEGETABLE OIL BASED POLYOLS AND POLYOLS MADE THEREFROM				
<b>INVENTOR(s)/APPLICANT(s) - Continued</b>				
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**PROVISIONAL APPLICATION FILING ONLY**

IMPROVED PROCESS TO MAKE VEGETABLE OIL BASED POLYOLS AND  
POLYOLS MADE THEREFROM

Field of the Invention

The invention relates to improved method of  
5 making vegetable based polyols for use in making  
polyurethane foams.

Background of the Invention

Polyurethanes are produced by the reaction of  
polyisocyanates and polyols. The first large scale  
10 commercial production of polyurethanes arose using  
polyester polyols from the ester condensation reaction of  
diols or polyols and dicarboxylic acids to make flexible  
foams. The polyester polyols were supplanted by  
polyether polyols because of lower cost and ability to  
15 make a wide range of polyols. Polyethers are made by  
polymerizing epoxides (oxiranes) derived from petroleum  
feedstocks with active hydrogen starting compounds  
(polyols and polyamines).

Rigid polyurethane foams have been made with  
20 castor oil or castor oil byproducts. Castor oil has been  
used in rigid foams because of its low molecular weight  
(short chain length) and high functionality (trihydroxyl).

Attempts have been made to make polyols from  
vegetable or renewable feedstocks such as those disclosed  
25 by Peerman et al., US. Patent Nos. 4,423,162; 4,496,487  
and 4,543,369. Peerman et al. describe a method reacting  
a hydroxyester monomer with a polyol or polyamine.  
However, Peerman et al., specifically describe problems of  
gelling, which can be avoided by limiting the extent of  
30 conversion or by using quantities of reactants far from

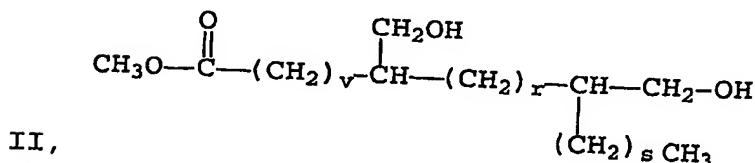
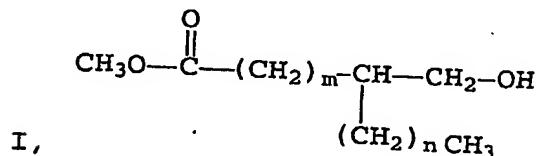
the amounts required stoichiometrically. Consequently, Peerman et al., only describe elastomers (crosslinked rigid polyurethanes) from their resultant polyols. In addition, secondary hydroxyls were described causing 5 sweating, wherein the product appears to be wet and not fully cured, thus limiting the use of low cost renewable initiators such as glycerol.

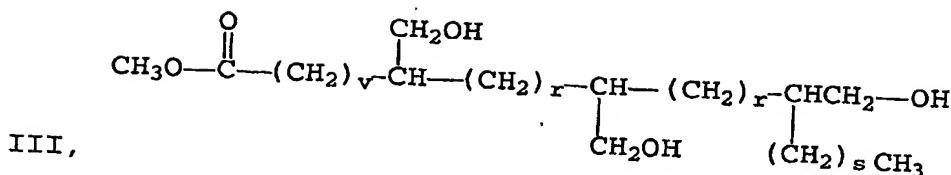
Accordingly, it would be desirable to provide both a formation method and a vegetable based polyol that 10 solves one or more of the problems of the prior art, such as one of those described above. In particular it would be desirable to provide a vegetable oil based (VOB) polyol that can be used to make flexible polyurethane foams in the absence of any other polyols.

15 Summary of the Invention

A first aspect of the invention is a process to make a vegetable oil based polyol, the process comprising,

20 i) mixing an initiator that is a polyol, polyamine, aminoalcohol or mixture thereof and a vegetable oil based (VOB) monomer having at least one of the formulae:





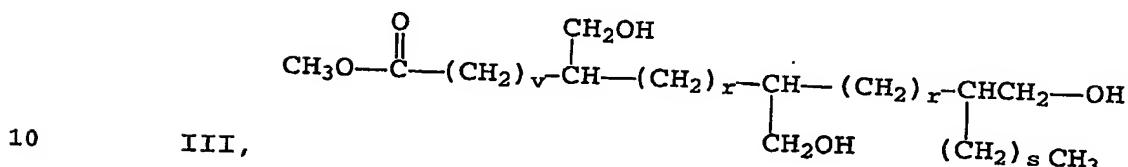
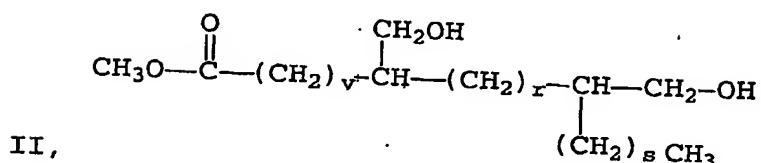
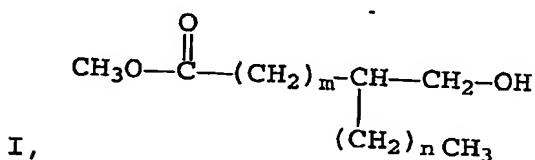
where  $m$ ,  $n$ ,  $v$ ,  $r$ , and  $s$  are integers and  $m$  is greater than 3,  $n$  greater than or equal to zero and  $m+n$  is from 11 to 19,  $v$  is greater than 3,  $r$  is greater than or equal to zero,  $s$  is greater than or equal to zero and  $v+r+s$  is from 10 to 18, and

ii) heating the mixture to a reaction temperature, for a reaction time, while under a vacuum and in the presence of an amount of catalyst sufficient to form the vegetable oil based polyol. It is understood that the initiator fails to contain an ester group that can transesterify under the reaction conditions.

The method of the first aspect surprisingly may form a non-gelled polyol with sufficient hydroxyl functionality and molecular weight to form a flexible foam when reacted with a polyisocyanate. The process even though performed under vacuum may use initiators that would volatilize off relative quickly at the reaction temperature used to form the VOB polyol. The process, surprisingly, makes novel non-gelled VOB polyols even when VOB monomers are present that have three hydroxyl groups. Finally, it has been surprisingly found that the process forms a unique VOB polyol, where all of the VOB monomer is reacted, but within the polyol there are some hydroxyl or amine groups of the initiator that have not been reacted even though the amount of VOB monomer is far in excess of the stoichiometric amount needed to react therewith.

A second aspect of the invention is a process to make a vegetable based polyol, the process comprising,

5 i) heating, in the presence of a catalyst a vegetable oil based monomer having at least one of the formulae:

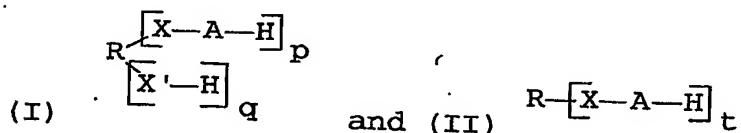


10 where m, n, v, r, and s are integers and m is greater than 3, n greater than or equal to zero and m+n is from 11 to 19, v is greater than 3, r is greater than or equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18 until some portion of the VOB monomers have reacted and subsequently

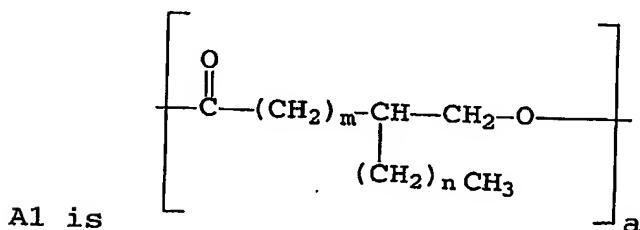
15 ii) introducing an initiator that is a polyol, polyamine, aminoalcohol or mixture thereof to the reacted VOB monomers of step (i) for a time and temperature, under 20 vacuum, sufficient to form the vegetable based polyol.

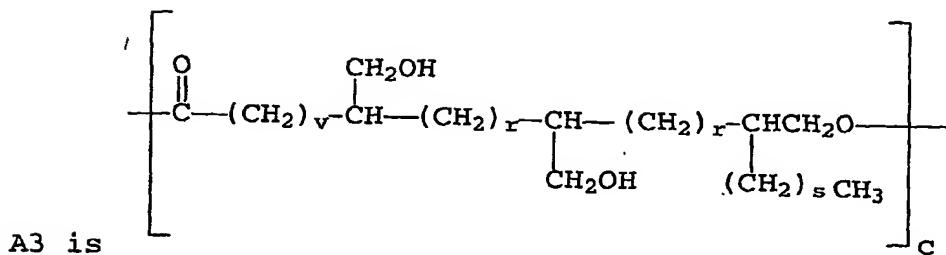
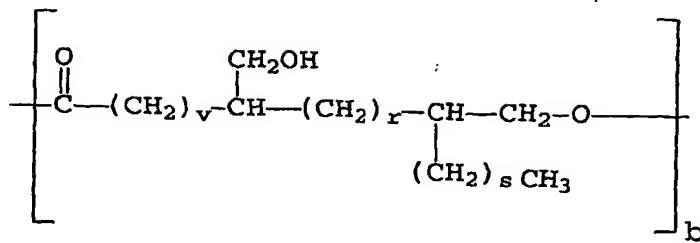
This aspect of the invention has been found to surprisingly make similar VOB polyols even though the initiator is added after the VOB monomers have, for example, built substantial molecular weight. The method 5 is believed to give improved control over the resultant molecular weight of the VOB polyol that is formed.

A third aspect of the invention is a vegetable oil based polyol comprised of



10 where R is a residue of a polyol, polyamine or aminoalcohol initiator; X and X' may be the same or different and is O, N or NH; p is an integer from 1 to 5; q is an integer from 1 to 5 wherein p + q is from 3 to 8, t is an integer from 3 to 8 and A may be the same or different and 15 is selected from the group consisting of A1, A2 and A3 where

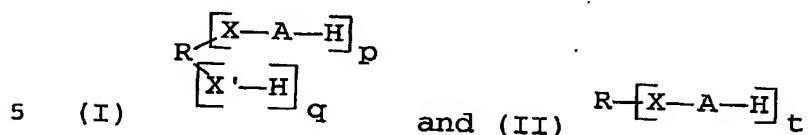




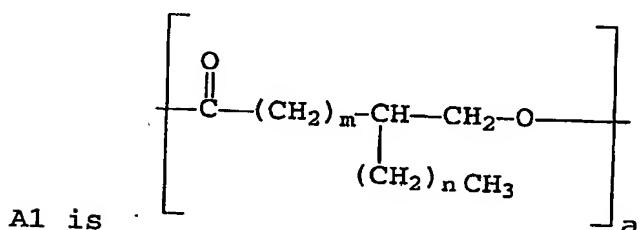
where m, n, v, r, s, a, b and c are integers and m is  
 5 greater than 3, n greater than or equal to zero and m+n is  
 from 11 to 19, v is greater than 3, r is greater than or  
 equal to zero, s is greater than or equal to zero and  
 v+r+s is from 10 to 18, a is from 0 to 35, b is from 0 to  
 10 35 and c is from 0 to 35, so long as that all a's, b's and  
 c's in any molecule of the vegetable oil based polyol are  
 not all zero and  $(a+b+c)/(p+q+t)$  is about 5 to about .100  
 in the vegetable oil based polyol. It is understood that  
 the each or all of the hydroxyls may react with the methyl  
 ester of another VOB monomer. As such, it is understood  
 15 that the structures shown above merely model the actual  
 degree of reaction (i.e., one VOB monomer hydroxyl  
 reacted). However, any or all of the available hydroxyl  
 groups are capable of reacting under the conditions of the  
 polymerization. That is to say, the growth of the chain  
 20 may occur not only at the hydroxyl site depicted in the  
 above structures, but, at any of the hydroxyls of the VOB  
 monomer. It is also conceivable that more than one of the

available hydroxyl groups of the VOB monomer may be acylated.

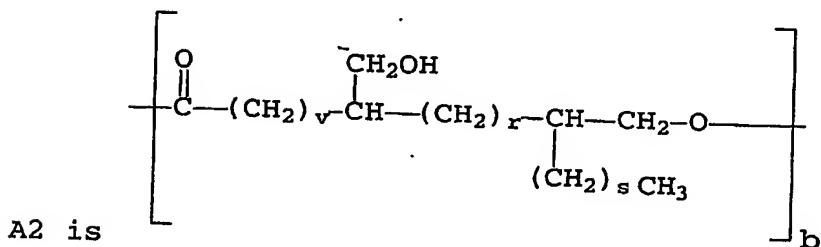
A third aspect of the invention is a vegetable oil based polyol comprised of

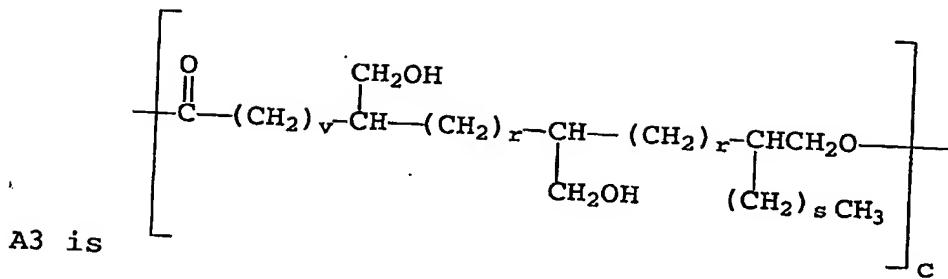


where R is a residue of a polyol, polyamine or aminoalcohol initiator; X and X' may be the same or different and is O, N or NH; p is an integer from 1 to 5; q is an integer from 1 to 5 wherein p + q is from 2 to 8, t is an integer from 2 to 8 and A may be the same or different and is selected from the group consisting of A1, A2 and A3 where



15



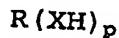


where m, n, v, r, s, a, b and c are integers and m is greater than 3, n greater than or equal to zero and m+n is from 11 to 19, v is greater than 3, r is greater than or equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18, a is from 0 to 35, b is from 0 to 35 and c is from 0 to 35, so long as that all a's, b's and c's are essentially not all zero, at least a portion of A is A3 and  $(a+b+c)/(p+q+t)$  is about 1 to about 100 in the vegetable oil based polyol.

The vegetable oil based polyols may be used in any applications that polyols are used. Examples include polyurethane applications of all types such as elastomers, coatings, adhesives, sealants, rigid foams and in particular flexible foams.

#### Detailed Description of the Invention

The vegetable based polyols of the present invention are made by reacting an initiator with a vegetable oil based (VOB) monomer. The initiator has at least one active hydrogen, which are reacted with the VOB monomer. The initiator may be depicted by the formula:

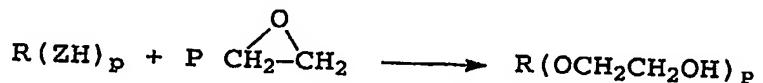


Where X is O, N, or NH and p is 1 to 8. In the formula, X may be the same or different. The initiator therefore encompasses polyols, polyamines and aminoalcohols. R

generally represents a linear, cyclic chain or combination thereof of alkane (C-C), alkene (C=C), ether (C-O-C) linkages or combinations thereof. The carbons within the aforementioned chain may be substituted with a methyl or ethyl group. Generally the molecular weight of the initiator is at most from 32 to about 2000. Preferably, the molecular weight is at least about 50, more preferably at least about 60, most preferably at least about 90 to preferably at most about 1400, more preferably at most about 1200 and most preferably at most about 800.

Exemplary polyol initiators include neopentylglycol; 1,2-propylene glycol; trimethylolpropane; pentaerythritol; sorbitol; sucrose; glycerol; alkanediols such as 1,6-hexanediol; 2,5-hexanediol; 1,4-butanediol; 1,4-cyclohexane diol; ethylene glycol; diethylene glycol; triethylene glycol; 9(1)-hydroxymethyloctadecanol, 1,4-bishydroxymethylcyclohexane; 8,8-bis(hydroxymethyl)tricyclo[5.2.1.0<sup>2.6</sup>]decene; Dimerol alcohol (36 carbon diol available from Henkel Corporation); hydrogenated bisphenol; 9,9(10,10)-bishydroxymethyloctadecanol; 1,2,6-hexanetriol; any of the aforementioned where at least one of the alcohol or amine groups present therein has been reacted with ethylene oxide, propylene oxide or mixture thereof; and combination thereof.

Any of the aforementioned where at least one of the alcohol groups present therein has been reacted with ethylene oxide or propylene oxide means the active hydrogen of the hydroxyl reacts to form a polyether polyol exemplified by the following formula:



where R is the same as defined above. It is also understood that the other alkoxylating agents instead of ethylene oxide or propylene oxide may be. Amine groups may also be reacted with the alkoxylating agent.

5           Exemplary polyamine initiators include ethylene diamine; neopentyldiamine, 1,6-diaminohexane; bisaminomethyltricyclodecane; bisaminocyclohexane; diethylene triamine; bis-3-aminopropyl methylamine; and triethylene tetramine.

10          Exemplary aminoalcohols include ethanolamine, diethanolamine, and triethanolamine.

Other useful initiators that may be used include polyols, polyamines or aminoalcohols described in U.S. Patent Nos. 4,216,344; 4,243,818 and 4,348,543 and British 15 Pat. No. 1,043,507.

Preferably, the initiator is selected from the group consisting of neopentylglycol; trimethylolpropane; pentaerythritol; sorbitol; sucrose; glycerol; 1,2-propylene glycol; 1,6-hexanediol; 2,5-hexanediol; 1,6-hexanediol; 1,4-cyclohexane diol; 1,4-butanediol; ethylene glycol; diethylene glycol; triethylene glycol; bis-3-aminopropyl methylamine; ethylene diamine; diethylene triamine; 9(1)-hydroxymethyloctadecanol; 1,4-bishydroxymethylcyclohexane; 8,8-bis(hydroxymethyl)tricyclo[5,2,1,0<sup>2,6</sup>]decene; Dimerol alcohol; hydrogenated bisphenol; 9,9(10,10)-bishydroxymethyloctadecanol; 1,2,6-hexanetriol; any of the aforementioned where at least one of the alcohol or amine groups present therein has been reacted with ethylene oxide, propylene oxide or mixture thereof; and combination thereof.

More preferably the initiator is selected from the group consisting of neopentylglycol; 1,2-propylene glycol; trimethylolpropane; pentaerythritol; ethoxylated pentaerythritol; propoxylated pentaerythritol; sorbitol;

5 sucrose; glycerol; ethoxylated glycerol; propoxylated glycerol; diethanolamine; alkanediols such as 1,6-hexanediol, 1,4-butanediol; 1,4-cyclohexane diol; 2,5-hexanediol; ethylene glycol; diethylene glycol, triethylene glycol; bis-3-aminopropyl methylamine;

10 ethylene diamine; diethylene triamine; 9(1)-hydroxymethyloctadecanol, 1,4-bishydroxymethylcyclohexane; 8,8-bis(hydroxymethyl)tricyclo[5.2.1.0<sup>2,6</sup>]decene; Dimerol alcohol; hydrogenated bisphenol; 9,9(10,10)-bishydroxymethyloctadecanol; 1,2,6-hexanetriol and

15 combination thereof.

Even more preferably the initiator is selected from the group consisting of glycerol; ethylene glycol; 1,2-propylene glycol; trimethylolpropane; ethylene diamine; pentaerythritol; diethylene triamine; sorbitol;

20 sucrose; or any of the aforementioned where at least one of the alcohol or amine groups present therein has been reacted with ethylene oxide, propylene oxide or mixture thereof; and combination thereof.

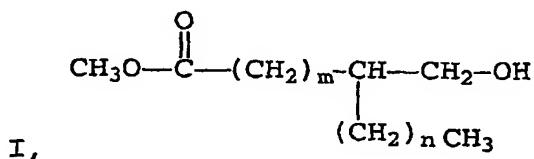
Most preferably the initiator is glycerol,

25 pentaerythritol, sucrose, sorbitol, an ethoxylated glycerol, propoxylated glycerol, ethoxylated pentaerthritol, propoxylated pentaerthritol or mixture thereof.

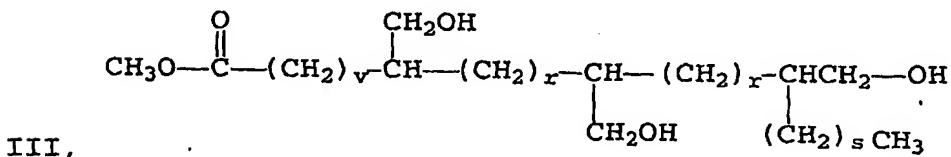
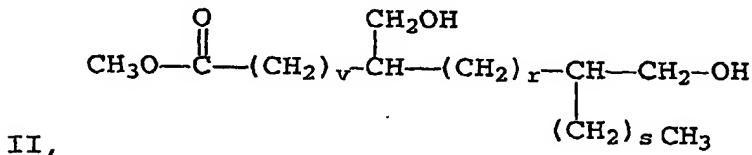
Surprisingly, using the method of the present invention, it is preferred that an initiator is used that has at least one secondary hydroxyl or secondary amine (e.g., glycerol). It is surprising, because the reaction

may cause the VOB monomer to react, for example with glycerol, in such a way that the resultant vegetable oil based polyol has at least some polyol molecules where at least one of the primary hydroxyls of the glycerol has not reacted with the VOB monomer, but the secondary hydroxyl has. This is further described below.

The VOB monomer is a vegetable oil based monomer having at least one of the formulae:



10



where m, n, v, r, and s are integers and m is greater than 15 3, n greater than or equal to zero and m+n is from 11 to 19, v is greater than 3, r is greater than or equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18.

The VOB monomer may be of any animal fat or 20 vegetable oil that is comprised of triglycerides that upon

saponification with a base such as aqueous sodium hydroxide yields a fatty acid and glycerol, where at least a portion of the fatty acids are unsaturated fatty acids (i.e., contain at least one carbon double bond).

5 Preferred vegetable oils are those that yield at least about 70% unsaturated fatty acids by weight. More preferably, the vegetable oil yields at least about 85%, more preferably at least 87%, and most preferably at least about 90% by weight unsaturated fatty acids.

10 It is understood that specific fatty acids derived from a vegetable oil, animal fat or any other source may be used. That is to say, for example, palmitoleic, oleic, linoleic, linolenic and arachidonic fatty acid alkyl esters may be used to form the VOB monomer directly. It is preferred

15 however to use a vegetable oil as previously described. Preferred vegetable oils include, for example, soy, safflower, cotton, linseed, peanut, olive, sunflower, canola, rapeseed, corn, palm or combination thereof. More preferably, the vegetable oil is a soy, sunflower, canola, corn, rapeseed oil, or combination thereof. Most preferably, the vegetable oil is soy, sunflower, canola or combination thereof. It is understood that the vegetable oil may be obtained from a genetically modified organism, such as genetically modified soybean, sunflower or canola.

25 The unsaturated fatty acid alkyl esters then may be formed, by any suitable process such as those known in the art, into the VOB monomer (hydroxymethylesters). For example, the hydroxymethyl group may be introduced by a hydroformylation process using a cobalt or rhodium

30 catalyst followed by the hydrogenation of the formyl group to obtain the hydroxymethyl group by catalytic or by chemical reduction. Procedures to form the hydroxymethylesters are described in U.S. Pat. Nos.

4,216,343; 4,216,344; 4,304,945 and 4,229,562 and in particular 4,083,816. Other known processes to form hydroxymethylesters from fatty acids may also be used such as described by U.S. Pat. Nos. 2,334,849 and 3,787,459.

5        In forming the VOB monomers, the formylated fatty acid alkyl esters may be completely formylated or only partially formylated. That is to say, the fatty acid alkyl esters of the particular vegetable oil may have some remaining unsaturated (C=C) bonds. Preferably, however,  
10      the amount of unsaturated bonds remaining after formylation is as described in concurrently filed application titled "ALDEHYDE AND ALCOHOL COMPOSITIONS DERIVED FROM SEED OILS," having inventors Donald Morrison et al., and attorney docket number 63104, incorporated  
15      herein by reference. After the fatty acid alkyl esters are formylated they are hydrogenated, such that there is desirably essentially no remaining unsaturated bonds (i.e., trace amounts at most and preferably no detectable amounts of unsaturation).

20       The VOB monomer and the initiator are mixed or blended together by any suitable means such as those known in the art. For example, simple stirring is sufficient.

25       The VOB monomer and initiator are heated to a reaction temperature, for a reaction time, while under a vacuum and in the presence of an amount of a catalyst sufficient to form the vegetable based polyol. The reaction temperature that is employed is, for example, a function of the VOB monomer, initiator and catalyst, but the reaction temperature is generally at least about 140°C  
30      to about 300°C when using a tin or titanium catalyst. Preferably, the reaction temperature is at least about 150°C, more preferably at least about 180°C, most

preferably at least about 190°C to preferably at most about 250°C, more preferably at most about 220°C and most preferably at most about 210°C.

5       The catalyst may be any suitable catalyst such as a tin, titanium, enzyme catalyst (e.g., lipase), carbonate catalyst (e.g., K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>) or combination thereof.

10      In a preferred embodiment, the catalyst is an enzyme catalyst, such as lipase, which allows the reaction temperature to be below about 100°C to about room temperature. This in turn allows the use of initiators (e.g., sugar) that would be degraded by the higher temperatures using tin or titanium catalysts.

15      The reaction time, similarly, is dependent on the variables described above for the reaction temperature. Generally, the time is at least about 10 minutes to at most about 24 hours. Preferably, the reaction time is at least about 15 minutes, more preferably at least about 30 minutes, more preferably at least about 1 hour to preferably at most about 12 hours, more preferably at most about 9 hours and most preferably at most about 5 hours.

20      To form the VOB polyol, it has been found that it is critical that the reaction be carried out under a vacuum. This is even true where the initiator is volatile at the reaction temperature. Volatile means that the initiator will volatilize off entirely in substantially less time than the total reaction time under the vacuum. For example, when the initiator is glycerol, the glycerol in the reaction vessel minus the VOB monomer would be volatilized off under a vacuum of about 20 torr in about

120 minutes at 200°C. Generally, the vacuum is at least about 100 torr. Preferably the vacuum is at least about 50 torr, more preferably the vacuum is at least about 20 torr.

5 In a preferred embodiment, particularly when using a volatile initiator, the VOB is placed in the reactor under vacuum at the reaction temperature for a period of time sufficient to transesterify a substantial amount of the VOB monomer (e.g., at least about 10% of the ester groups  
10 of the VOB monomer have undergone transesterification) and subsequently the initiator is added to form the VOB polyol. This method allows for precise control of the molecular weight without substantial loss of a volatile initiator.

15 The amount of catalyst has also been found to be critical when using a tin or titanium catalyst solely. This is particularly true when the initiator is volatile as described previously. The amount of catalyst must be some minimum amount to effect the reaction between the  
20 initiator and VOB monomer sufficiently quickly to realize the VOB polyol. The amount of catalyst depends, for example, on the particular type of catalyst, VOB monomer, and initiator.

25 Generally, when a tin catalyst is employed, the amount of catalyst is at least about 100 ppm to at most about 2500 ppm by weight of tin to the total reaction mixture. Preferably, the amount of tin catalyst is at least about 250 ppm, more preferably at least about 500 ppm and most preferably at least about 1000 ppm to  
30 preferably at most about 2000 ppm, more preferably at most about 1500 ppm. The tin catalyst may be any suitable such as those known in the art. Exemplary tin catalysts

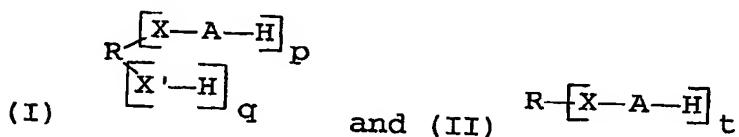
include tin (II) octanoate, tin (II) 2-ethylheptanoate, dibutyl tin (IV) dilaurate, and other tin catalysts which are similarly functionalized. Preferably the tin catalyst is tin (II) octanoate, tin (II) 2-ethylheptanoate, or dibutyl tin (IV) dilaurate.

Generally, when a titanium catalyst is employed, the amount of catalyst is at least about 100 ppm to at most about 2500 ppm by weight of titanium to the total reaction mixture. Preferably, the amount of titanium catalyst is at least about 250 ppm, more preferably at least about 500 ppm and most preferably at least about 1000 ppm to preferably at most about 2000 ppm, more preferably at most about 1500 ppm. The titanium catalyst may be any suitable such as those known in the art.

Exemplary titanium catalysts include titanium tetraisopropoxide, titanium tetraisobutoxide, or any appropriately functionalized titanium (IV) alkoxide. Preferably the titanium catalyst is titanium tetraisopropoxide.

The ratio of VOB monomer to initiator reactive groups is generally at least a stoichiometric amount. (i.e., if the initiator is 1 mole of glycerol, the amount of VOB monomer is at least 3 moles) to at most about 100. Preferably the ratio of VOB monomer to initiator reactive groups is at least 2, more preferably at least about 5, even more preferably at least about 7 and most preferably at least about 10, to preferably at most about 50, more preferably at most about 25, and most preferably at most about 20. It has been surprisingly found when using these higher ratios even when reacting with a VOB monomer having 3 hydroxy group monomers therein a VOB polyol may be formed that is non-gelled and even a liquid.

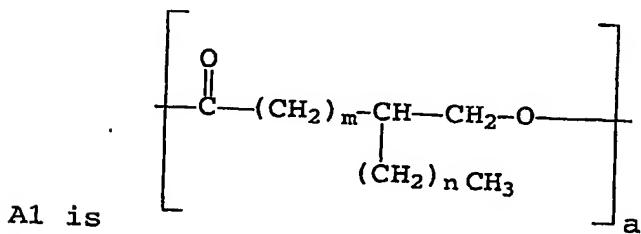
When employing the method of the present invention, it has been surprisingly discovered that a VOB polyol may be formed that has at least a portion of the polyol being comprised of a polyol molecule that has at least one initiator reactive group that is unreacted even while the VOB polyol as a whole has a VOB monomer to initiator reactive site ratio of at least 5. That is to say, the VOB polyol is comprised of

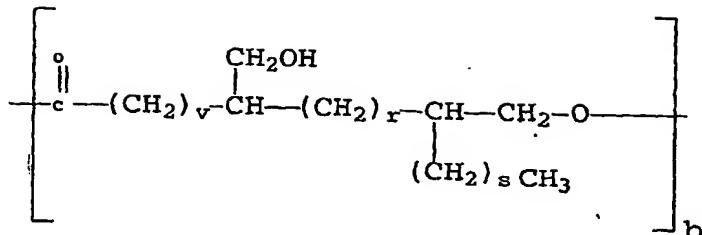


where

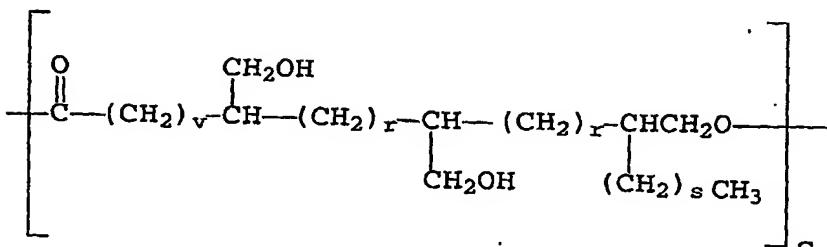
R is a residue of a polyol, polyamine or aminoalcohol initiator;

X and X' may be the same or different and is O, N or NH; p is an integer from 1 to 5; q is an integer from 1 to 5  
 15 wherein p + q is from 3 to 8, t is an integer from 3 to 8 and A may be the same or different and is selected from the group consisting of A1, A2 and A3 where





A2 is



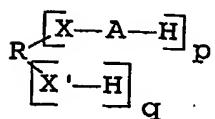
A3 is

where m, n, v, r, s, a, b and c are integers and m is  
 5 greater than 3, n greater than or equal to zero and m+n is  
 from 11 to 19, v is greater than 3, r is greater than or  
 equal to zero, s is greater than or equal to zero and  
 v+r+s is from 10 to 18, a is from 0 to 35, b is from 0 to  
 10 35 and c is from 0 to 35, so long as that all a's, b's and  
 c's in any molecule of the vegetable oil based polyol are  
 not all zero and  $(a+b+c)/(p+q+t)$  is about 5 to about 100  
 in the vegetable oil based polyol. The  $(a+b+c)/(p+q+t)$   
 ratio is indicative of the VOB monomer to initiator  
 reactive group ratio.

15 In a preferred embodiment, the VOB polyol has a  
 least a portion of the polyol being comprised of A3  
 constituent. This particular embodiment, is preferred  
 because it allows the polyol to realize a sufficient  
 hydroxyl functionality while achieving a sufficient  
 20 molecular weight for use to make flexible polyurethane  
 foams using VOB polyol as the sole polyol reacted with an  
 isocyanate to form the polyurethane foam. Preferably, the

amount of the A3 constituent in the VOB polyol is at least about 0.01 weight percent of the total VOB polyol, more preferably the amount is at least about 0.02 weight percent, most preferably at least about 0.05 weight percent to preferably at most about 25 weight percent, more preferably at most about 20 weight percent and most preferably at most about 10 weight percent of the VOB polyol.

In another preferred embodiment when employing an initiator having, for example, a secondary hydroxyl or amine, the VOB polyol may have a portion of the VOB polyol that has a structure



where at least one X'-H group is a primary hydroxyl or primary amine and at least one X-A-H is located at a position corresponding to a secondary hydroxyl or secondary amine of the initiator. Preferably, the VOB polyol is at least partially comprised of the above structure where all of the X'-H groups are a primary hydroxyl or primary amine and all of the X-A-H groups are located at a position corresponding to a secondary hydroxyl or secondary amine of the initiator.

The VOB polyol may be used to make polyurethanes by reacting it with a polyisocyanate such as those known in the art using known methods to make such polyurethanes. Preferably the polyurethane is a flexible foam. More preferably the polyurethane is a flexible foam that has been formed by reacting the VOB polyol with a

polyisocyanate in the absence of any other polyol. That is to say the VOB polyol is the sole polyol that is used to make the flexible foam.

Generally the VOB polyol may have a weight  
5 average molecular weight of about 350 to about 10,000. Preferably the weight average molecular weight is at least about 500, more preferably at least about 1000 and most preferably at least about 1500 to preferably at most about 10,000, more preferably at most about 6000 and most  
10 preferably at most about 3000. It is preferred that the VOB polyol is a liquid and surprisingly the method employed is capable of making high molecular weight polyols without gellation.

VOB polyols of the invention may be used with  
15 any of the additives commonly known in the art for the production of polyurethane polymers. Any of a range of additives such as blowing agents, catalysts, surfactants, cell openers, colorants, fillers, load bearing enhancement, additives such as copolymer polyols, water, internal mold  
20 releases, antistatic agents, antimicrobial agents, and other additives known to those skilled in the art are useful within the scope of the invention.

While the full range of surfactants which are typically used in the formation of polyurethane foams are  
25 useful in the scope of the invention, certain surfactants are preferred for foams which have high percentages of vegetable based polyols as the polyol component of the foam formulation. In particular, in the formation of flexible slabstock foam, high efficiency alkoxylsilane  
30 surfactants such as those commonly used in specialty grades of flexible foam such as low-resiliency or "visco-elastic" foam are unexpectedly found to greatly enhance

the properties of flexible slabstock foams made when 100% of the polyol side of the foam is made from VOB polyol. Surfactants which are preferred are those such as L626 available from Crompton Corporation or other polyol

5 pendant chains grafted with silicone moiety. Property enhancements are observed in properties such as foam cell size, cell structure, foam feel or "hand," which is defined as the aesthetic feel or tactile quality of the foam, that indicates its fineness, texture, and,

10 durability, and foam porosity. The preferred surfactants result in slabstock foam products from 100% VOB polyol which have such properties comparable to slabstock foams prepared from 100% conventional commercial-grade EO/PO polyols.

15 It also has been found that the VOB polyols of this invention may form polyurethane foams made with a wide range of water concentrations. Generally, the water concentrations may range from about 1 part per hundred parts to about 10 parts per hundred parts of polyol by weight. Preferably, the water concentration is at least about 2, more preferably 3 and most preferably at least about 4 to preferably at most about 9, more preferably at most 8 and most preferably at most about 6 parts per hundred parts of polyol by weight.

20

25

#### EXAMPLES

##### EXAMPLES 1-27. Methods for Producing Polyols from Vegetable Oil Based Fatty Acid Methyl Esters

Hydroxymethylated fatty acid methyl esters of soybean oil and 9,(10)-hydroxymethyl stearate (from methyl oleate) are produced according to the procedure described in concurrently filed application titled aldehyde AND ALCOHOL Compositions Derived from Seed Oils," having inventors

Donald Morrison, et al., attorney docket number 63104 described previously.

Glycerol was obtained from the Sigma-Aldrich Chemical Company "(CAS# [56-81-5]) and distilled under vacuum at 5 20mm/183°C. Distilled glycerol was then stored under nitrogen until used.

CEI-625 is a glycerol initiated EO polyol with a number average molecular weight of 625. It is produced at The Dow Chemical Company.

10 Trimethylolpropane [77-99-6] is obtained from the Sigma-Aldrich Chemical Co.

1,6-hexanediol [629-11-8] is obtained from the Sigma-Aldrich Chemical Co.

15 CEI-1200 is a glycerol initiated EO polyol with a number average molecular weight of 1200. It is produced at The Dow Chemical Company.

PE-270 is a pentaerythritol based polyol which has been ethoxylated with ethylene oxide to a number average molecular weight of 270. PE-270 is available from Aldrich 20 Chemical Company of Milwaukee, WI.

Tetrol 600 is pentaerythritol which has been ethoxylated to a number average molecular weight of 600. It was prepared at the Dow Chemical Co.

25 Tetrol 800 is pentaerythritol which has been ethoxylated to a number average molecular weight of 800. It is available from Sigma Aldrich Chemical company of Milwaukee, WI, and is sold as pentaerythritol ethoxylate [30599-15-6].

Sucrose [57-50-1] is obtained from the Imperial Sugar Co.

D-Sorbitol [50-70-4] is obtained from the Sigma Aldrich Chemical Co.

Pentaerythritol [115-77-5] is obtained from the Sigma  
5 Aldrich Chemical Co.

N-methylpyrrolidinone (NMP) [872-50-4] is obtained from  
the Sigma Aldrich Chemical Co.

Diethylene Glycol [111-46-6] is obtained from the Sigma  
Aldrich Chemical Co.

10 Voranol 370 is a mixture of sucrose and glycerol propoxylated to a MW of ~800. It has an average functionality of 6.85, and is obtained from the Dow Chemical Co.

Potassium Carbonate [584-08-7] is obtained from the Sigma  
15 Aldrich Chemical Co.

Ethylene Diamine [107-15-3] is obtained from the Sigma Aldrich Chemical Co.

Vanox 945 is an antioxidant package available from RT  
Vanderbilt Co. Inc. It is a mixture of 60-70%  
20 benzeneamine, -N-phenyl-, reaction product with 2,4,4- trimethylpentene and 2-methylpropene [184378-08-3], 20-25% tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)methane [6683-19-8], 9% petroleum process oil, <3.0% DMS extractable material [64742-52-5],  
25 <1% diphenylamine [122-39-4], 1% phenothiazine [92-84-2].

Irganox 5057 is benzeneamine, -N-phenyl-, reaction product with 2,4,4-trimethylpentene [68411-46-1] available from Ciba Co.

Tin (II) Octanoate [301-10-0] is available from City Chemical Co.

Ti (IV) isopropoxide [546-68-9] is obtained from the Sigma Aldrich Chemical Co.

5 Stannous Octanoate [301-10-0] is available from City Chemical Co.

Calcium acetate [62-54-4] is obtained from Sigma Aldrich Chemical Co.

10 Tin (II) ethyl hexanoate [301-10-0] is obtained from Sigma Aldrich Chemical Co.

Dibutyltin dilaurate [77-58-7] is available from Sigma Aldrich Chemical Company of Milwaukee, WI.

15 Lipase catalyst is derived from *candida antarctica* and is supported on acrylate beads. This polymer-supported lipase catalyst is available from Sigma Aldrich Chemical Company of Milwaukee, WI.

Hydroxyl equivalent weight analysis is performed by the Olin Titration method.

20 Percent acidity is measured by the ASTM test method designation D 4662-93.

Molecular weight values (M<sub>n</sub>, M<sub>w</sub>, M<sub>z</sub>, M<sub>p</sub>, P.D) are measured by gel permeation chromatography using Polymer Labs PL Gel columns and polyethylene oxide or polystyrene standards.

25 Examples 1-17. A general polymerization procedure for seed oil polyols produced from fatty acid methyl esters

Hydroxymethylated fatty acid methyl ester monomer was transferred into a three-necked reaction flask between 500

ml and 5000 ml in capacity, the choice of which is commonly known to those skilled in the art and is dependent on the amount of starting materials used. The reactor was equipped with a mechanical stirrer, packed 5 condenser, nitrogen purge, heating mantle with thermowatch and a thermometer. A vacuum line equipped with a dry ice trap and vacuum regulator was attached. Initiator and monomer were added and the contents of the reactor stirred and degassed while heating to 50 degrees under 20 torr 10 vacuum. Once the temperature was stable, catalyst was added and the temperature was increased to the final specified reaction temperature. The initial setting for the vacuum was started at 100 torr and the pressure was decreased slowly to 5-20 torr. Heating was continued at 15 the specified reaction temperature until methanol loss was no longer visible, usually at least about 1 hour, and no more than 28 hours. Heating was continued and a slow flow of nitrogen was added through the nitrogen purge. Polymerization was allowed to continue for at least 1 hour 20 and no more than 28 hours. In some specified cases an antioxidant such as Vanox 945 or Irganox 5057 was added just before the fluid polymer is transferred to a glass jar under nitrogen.

The following tables describe the recipes used to produce 25 polyols of the invention. The following examples of the invention are meant to illustrate but not limit the scope of the invention. In all tables, the term "M/I ratio" is meant to indicate the molar ratio of hydroxymethylated fatty acid methyl ester monomer to the initiator. The 30 catalysts are identified according to the following designations: Sn(II) is stannous octanoate; Sn(IV) is dibutyl tin dilaurate; Ti(IV) is titanium tetrakisopropoxide; Ca is calcium acetate.

Examples 1-10. Polyols produced from 9(10)-Hydroxymethyl Stearate

Polyols were produced from 9, (10)-hydroxymethyl stearate using the specified initiator and catalyst using the above 5 procedure and as detailed in the below Table I.

Table I: Examples 1-10 Polyol Properties and Run Conditions:

Example #	Initiator (moles)	Initiator Name	M/I mole ratio	Catalyst (PPM)	Temp (deg C)	Run Time (hr)	Viscosity (cp at 25C)	Acidity (meq/g)	Hydroxyl %	Hew	M <sub>D</sub>	M <sub>n</sub>	M <sub>w</sub>	PD
1	0.483	Glycerol	8.38	Sn(II) 996	205	27	260	0.0145	4.209	404	430	786	1210	1841
2	0.2463	Trimethylol propane	1.5	Sn(II) .97	210	14	--	--	1.49	1140	7863	4125	10,222	19,111
3	0.0337	1,4-Hexanediol	9.04	Sn(II) 2400	210	14	--	--	1.62	1047	8617	5088	13,217	25233
4	0.757	CEI-1200	4.68	Sn(II) 1000	205	4	3410	0.0112	2.088	814	4200	2937	4427	6192
5	0.422	CEI-625	6.99	Sn(II) 195	12	6100	0.0064	2.3674	718	5281	2847	4823	7035	1.69
6	0.6223	CEI-625	6.51	Sn(II) 1012	205	24	2920	0.00168	1.999	850	5440	3118	5295	7473
7	0.6243	CEI-625	6.48	Ti(IV) 1018	205	3	4540	0.0030	2.123	801	4451	2893	4524	6340
8	0.6234	CEI-625	6.54	Sn(IV) 995	205	1	2420	0.0023	1.837	925	3803	2629	3591	4573
9	0.4049	CEI-625	10.0	Ca 2494	205	27	3170	0.00392	1.746	974	5073	2967	5248	7552
10	0.060	Tetrol 800	5.09	Ti(IV) 1000	205	14	2790	--	2.56	663	5678	3073	6189	11,675
														2.01

Examples 11-18. Polyols produced from hydroxymethylated fatty acid methyl esters of vegetable oils

The vegetable oil based polyols were produced using the above general procedure from the hydroxymethylated fatty acid methyl esters of soybean oil and these polyols are shown in the below Table II.

Table II: Example 11-18 Properties and Reaction Conditions:

Example #	Initiator (moles)	Initiator Name	M/I mole ratio	Catalyst (PPM)	Sn(II) mole ratio	Temp (deg C)	Run time (hr)	Viscosity (cP at 25C)	Acidity (meq/g)	Hydroxyl %	HEW	Mp	Mn	Mw	Mz	PD
11	0.395	CEI-625	7.96	Sn(II) 1188	195	12	5140	0.0030	2.02	841	4472	2959	5018	6770	1.70	
12	0.523	CEI-625	5.98	Sn(II) 1365	195	12	4100	0.00248	2.254	754	4009	2615	4342	6413	1.66	
13	0.512	CEI-625	5.95	Sn(II) 891	195	6	2730	0.00064	1.881	904	3118	2347	3612	5185	1.54	
14	0.404	Tetrol 600	9.98	Sn(II) 995	205	3	2680	0.0086	1.512	1124	4643	2877	4595	6410	1.60	
15	1.445	CEI-625	6.03	Sn(II) 701	195	10	3450	0.00143	2.2524	755	3977	2858	4304	6065	1.51	
16	0.637	CEI-625	5.99	Sn(II) 827	195	12	3720	0.0059	2.233	761	4000	2687	4270	6152	1.59	
17	2.09	PE-270	1.0	Sn(II) 1097	195	9	4100	0.0037	11.67	145	1082	1053	1450	2014	1.38	
18	1.25	CEI-625	1.55	Sn(II) 1034	195	10	1160	0.00401	5.22	325	1299	1491	2047	2861	1.37	

Examples 19-22. Large scale preparation of vegetable oil based polyols using CEI-625 initiator and stannous octanoate catalyst:

Hydroxymethylated methyl esters of soybean oil and CEI-625 were combined in a reactor with stirring, and the oxygen was purged from the reactor by pulling a vacuum on the reactor and refilling the reactor with nitrogen. Catalyst (stannous octanoate) was added to the reactor and agitation was continued. A slow nitrogen sparge was fed to the reactor and the mixture was heated to 205°C while maintaining a vacuum of 80 torr. The heating was continued for a minimum of 4 hours under a constant vacuum with a slow nitrogen sweep. The mixture was cooled to 62°C and the antioxidant Irganox 5057 (121 grams) was added with continuing agitation.

In the following examples, FAME indicates the source of the fatty acid methyl ester used for the polymerization, with HMS indicating hydroxymethyl stearate and Soy indicating hydroxymethylated soybean oil. The catalyst Sn(II) is stannous octanoate. The properties and reaction conditions of the polyols of Examples 19-22 are shown in Table III.

Table III: Properties and Reaction Conditions of Examples 19-22

Example #	NAME kg	Initiator CEI-625 Kg	N / I mole ratio	Catalyst PPM Sn(II)	Temp (deg C)	Run time (hr)	Viscosity (cp at 25C)	Acidity (meq/g)	Hydroxyl %	HEW	Mp	Mn	Mw	Pd	
19	HMS 38.83	11.39	10:1	1002	225	4.5	2800	0.00354	2.06	825	5136	3121	5179	1.6456	
20	HMS 70.31	20.59	10:1	Sn(II) 1000	205	4	3010	0.000713	2.0421	832	4970	3015	5039	7072	1.6713
21	Soy 26.15	11.8	6:1	Sn(II) 1005	195/20	12	3940	0.002	2.256	772.30	4040	2669	4367	6403	1.64
22	Soy 26.15	11.8	6:1	Sn(II) 1000	195/20	12	3570	0.00489	2.363	779.56	3925	2578	4293	6409	1.67

Examples 23-24. Lipase-catalyzed, saccharide-initiated polyols

Hydroxymethylated fatty acid methyl ester monomer prepared from soybean oil was transferred into a three-necked 5 reaction flask between 1000 ml and 5000 ml in capacity, the choice of which is commonly known to those skilled in the art and is dependent on the amount of starting materials used. The reactor was equipped with a mechanical stirrer, packed condenser, nitrogen purge, 10 heating mantle with thermowatch and a thermometer. A vacuum line equipped with a dry ice trap and vacuum regulator was attached.

The reactants (monomer and initiator) were weighed into the flask and heated to 50°C under 20 torr vacuum. 15 Following this degassing step, the catalyst (0.5 g) was added. The reactor was maintained at 50°C at 20 torr vacuum for 6 hours. Then the reactor was heated to 60°C under 20 torr vacuum and held there for 12 more hours. The reactor was cooled to 50°C and the product filtered 20 through a funnel with a plug of glass wool. The product solidified on standing at room temperature and this polyol's properties and reaction conditions are shown in Table IV.

Table IV: Properties and Reaction Conditions of Examples 23 and 24.

Example #	Initiator (moles)	Initiator Name	M / I Mole ratio	Lipase Catalyst (g)	Temp (deg C)	Run Time (hr)	Viscosity (cp at 25C)	Acidity (meq/g)	Hydroxyl %	MW	Mn	Mw/Mn	Mz	PD	
23	0.0786	Glycerol / Sucrose	1.49	0.50	50	42	5300	0.0356	8.110	209.6	836	1126	1454	2542	1.29
24	0.0672	Glycerol	8.34	0.50	50	42	592	0.00643	3.563	477.1	800	1207	1504	1954	1.25

Examples 25-26. Saccharide-initiated seed oil polyols produced with NMP cosolvent

Hydroxymethylated fatty acid methyl ester monomer derived from soybean oil was transferred into a three-necked reaction flask between 1000 ml and 5000 ml in capacity. The reactor was equipped with a mechanical stirrer, packed condenser, nitrogen purge, heating mantle with thermowatch and a thermometer. A vacuum line equipped with a dry ice trap and vacuum regulator was attached. The reactants (monomer and initiator) were weighed into the flask and heated to 195°C under 20 torr vacuum. The system was maintained at this temperature for 3 hours during which time water was removed from the system. The system was heated to 195°C under 20 torr vacuum for 5 hours to remove the remainder of the water.

The system was opened and 0.71 gram of catalyst was added. The reactor was heated to 195°C under 20 torr vacuum and held there for 6 hours. The reactor was cooled to 170°C and 522 grams of NMP and another 0.71 gram catalyst charge was added. The temperature was maintained for 2 hours. Then 40 g of potassium carbonate was added and the vacuum was maintained at 100 torr. The temperature was maintained for 3 hrs. The reactor contained a clear dark amber very viscous liquid. The NMP was removed. After no more NMP could be removed the reactor was shutdown and left at 80°C to avoid solid formation. The reactor was heated to 180°C and slowly dumped through a funnel containing a plug of glass wool to remove any solid carbonate. A heat lamp was necessary to keep the liquid flowing. In these Examples, the catalysts Sn(II) was stannous octanoate. The properties and run conditions for Examples 25 and 26 are shown in Table V.

Table V: Properties and Run Conditions of Examples 25 and 26.

Example #	Initiator (moles)	Initiator Name	M/I Mole ratio	Catalyst (PPM) Sn(II)	Temp (deg C)	Run time (hr)	Viscosity (cp at 25C)	Acidity (meq/g)	Hydroxyl %	Mp	Mn	Mw	Mz	PDI
25	0.98	Sorbitol	3.0	1204	195	8	>196000	0.01007	7.064	240	5856	2750	4885	7433 1.78
26	1.90	Penta-erythritol	2.0	942	205	10	>196000	0.00335	6.223	273	1213	2904	4542	6670 1.56

Examples 27-28. Seed oil polyols produced with  
Sn(II)/K<sub>2</sub>CO<sub>3</sub> cocatalysts

In the following examples the catalysts are identified according to the following designations: Sn(II) is 5 stannous octanoate, and K<sub>2</sub>CO<sub>3</sub> is potassium carbonate.

Hydroxymethylated fatty acid methyl ester monomer was transferred into a three-necked reaction flask between 1000 ml and 5000 ml in capacity, the choice of which is commonly known to those skilled in the art and is 10 dependent on the amount of starting materials used. The reactor was equipped with a mechanical stirrer, packed condenser, nitrogen purge, heating mantle with thermowatch and a thermometer. A vacuum line equipped with a dry ice trap and vacuum regulator was attached.

15 The reactants (monomer and initiator) were weighed into the flask and heated to 90°C under 100 torr vacuum. After 30 minutes, the vacuum was broken and K<sub>2</sub>CO<sub>3</sub> was added. The reactor was heated to 120°C under 100 torr vacuum, and after 1 hr the stannous octanoate was added. The pressure 20 was decreased to 50 torr and the system became visibly viscous and slightly yellow after 6 hrs. The reactor was heated to 60°C and the product was transferred to a storage container.

Table VI: Properties and Conditions of Examples 27 and 28.

Example #	Initiator (moles)	Initiator Name	N/I Mole ratio	K <sub>2</sub> CO <sub>3</sub> / Sn(II) Catalyst (PPM)	Temp (deg C)	Run time (hr)	Viscosity (cP at 25C)	Acidity (meq/g)	Hydroxyl %	MW	Tg	Mz	PD
27	1.14	Voranol 370	0.90	4699/50 9 <sub>9</sub>	90-110	6	2680	0.00081	9.338	182	831	795	82.6
28	1.02	Diethylene Glycol	2.93	7040/59 8	120	6	3230	--	4.075	417	3573	2823	4064

Example 29. Seed oil polyol produced from amine-containing initiator

5

The hydroxymethylated fatty acid methyl ester mixture derived from soybean oil (soy monomer) (100 g) was transferred into a 250-ml three-neck flask equipped with a magnetic stirrer, condenser/nitrogen purge with moisture trap, a heating mantle with thermowatch and a thermometer. Ethylenediamine (9.12 g) was added and heated to 140°C, under N<sub>2</sub>. Once the temperature was stable, Tin (II) 2-ethylhexanoate catalyst (0.1133 g) was added and the polymerization was stirred overnight. The nitrogen line was then replaced with a vacuum line. Vacuum was gradually drawn down to 50 torr. The reaction is monitored periodically to insure the vacuum is stable. The polymerization is continued overnight. The vacuum was removed and the polyol was cooled and collected. The polyol at 25°C was a solid and the Mp, Mn, Mw, Mz and PD of the polyol was 955, 1034, 1316, 1598 and 1.27.

Example #30. Seed oil polyol produced with a different order of addition of the monomer and initiator

25 The VOB monomer (The hydroxymethylated fatty acid methyl ester mixture derived from soybean oil) only was weighed (8.5 moles) into the flask and the reactor was heated under 20 torr vacuum to 50°C. Following the degassing the vacuum was broken and 1.58 g of catalyst (tin II Octanoate) was added and the system heated to 195°C. The reaction was closely monitored to make sure that the homopolymerization was not allowed to go so far as to gel.

After 4 hrs, the solution was noticeably viscous even at 195°C, the reactor was shutdown, sampled, and left under nitrogen overnight. CEI-625 initiator was weighed (1.38 moles) into the flask and the reactor heated to 195°C  
 5 under 20 torr vacuum. The solution was noticeably turbid even after heating. After about 2 hours at 195°C, the system had cleared and the solution was much less viscous. After about 8 hours the reactor was cooled to 100°C and 9.1 grams of Irganox 1076 and 5.1 grams of Vanox 945 were  
 10 added and the polyol was collected into a glass storage container. The properties of this Polyol appear in Table VII.

Table VII: Properties of Example 30

Example #	Viscosity (cP at 25C)	Acidity (meq/g)	Hydroxyl %	HEW	Mp	Mn	Mw	Mz	PD
30	3440	0.00323	2.573	660	4725	3163	4560	6184	1.44

15

Examples 31-67. Methods for production of polyurethanes from seed oil polyols:

All foam samples are prepared in a consistent manner  
 20 according to the following general procedure.

Chemical components which are used for the preparation of flexible and rigid polyurethane foams include but are not limited to:

Diethanolamine (DEOA) is a molded foam crosslinker which  
 25 is available from the Dow Chemical Co.

Dabco 33LV is a 33% crystalline diethylenetriamine in 67% dipropylene glycol. It is a molded foam catalyst which is available from Air Products and Chemicals, Inc.

Dabco DC 5164 is a molded foam silicone surfactant which is available from Air Products and Chemicals, Inc.

Tegostab-b8708 a molded foam silicone surfactant which is available from Degussa Goldschmidt Chemicals Corp.

5 Niax A-400 is a molded foam amine catalyst consisting of 40% tertiary amine/carboxylic salt (trade secret), 40% water, 20% bis (2-dimethylaminoethoxy)ether, and 4% hydroxyl compound (trade secret). Available from Crompton OSI Specialties Co.

10 Niax A-300 is a molded foam amine catalyst consisting of 40% tertiary amine/carboxylic salt (tradesecret), 20% triethylenediamine, and 40% water, available from Crompton OSI Specialties Co.

15 Polycat 58 is a proprietary composition amine catalyst used in molded foams, available from Air Products and Chemicals.

Polycat 5 is pentamethyl diethylene triamine. A rigid foam catalyst which is available from Air Products and Chemicals, Inc.

20 Polycat 8 is N,N-dimethyl cyclohexylamine. A rigid foam catalyst which is available from Air Products and Chemicals, Inc.

DC-5160, a flexible slabstock foam silicone surfactant is available from Air Products & Chemicals, Inc.

25 L-626 is a low-resiliency viscoelastic flexible slabstock foam surfactant available from Crompton Corp.

D-8264, is an optimized amine catalyst blend for slabstock foam available from Air Products & Chemicals, Inc.

Water used for these formulations is distilled, deionized water.

T-95, which is stannous octanoate catalyst, 33% by weight in dioctylphthalate is available from Air Products and

5 Chemicals, Inc.

Voranol 3137A, which is a 2.7 average functional, 13 wt. % ethylene oxide, heterofed 3100 MW polyol which is available from The Dow Chemical Company.

10 Voranol 3943A, which is an 1807 equivalent weight copolymer polyol based on Voranol 3136 (A 3100 MW 13% EO heteroclear polyol) and 43 wt. % styrene/ acrylonitrile solids, is available from The Dow Chemical Company.

15 Voranol 3512: A 2.7 functional, 3500 MW 13% wt. % ethylene oxide, heterofed polyol, is available from The Dow Chemical Company.

Voranol 3010, which is a 2.8 functional, 3000 MW 8% ethylene oxide heterofed polyol, is available from The Dow Chemical Company.

20 Voranol 3022J, which is a 2.6 functional, 3000 MW all propylene oxide polyol, is available from The Dow Chemical Company.

Specflex NC-632 is a 4.7 functional, propylene oxide block plus 15% ethylene oxide capped 1750 EW polyol used in flexible molded foam. Available from the Dow Chemical Co.

25 Specflex NC-700 is a 40% solids (styrene-acrylonitrile) copolymer polyol based on Voranol 4735 (a 3.0 functional, propylene block plus 17% ethylene oxide capped polyol with a 1580 equivalent weight) used in flexible molded foams.

Nominal equivalent weight is 2600. Available from the Dow Chemical Co.

Voranol 3136: A 2.7 average functionality, 13 wt. % ethylene oxide heterofed 3100 MW polyol used to make 5 slabstock foam. Available from the Dow Chemical Co.

Voranol CP 1421: A 2.94 average functionality, 80% ethylene oxide heterofed 5000 MW polyol used in flexible slab and molded foams which is available from the Dow Chemical Co.

10 DABCO T-9 is stabilized stannous octanoate, a catalyst used in flexible slabstock foams, available from Air Products and Chemicals, Inc.

VORANATE T-80 is type I TDI (toluene diisocyanate) with an equivalent weight of 87. Used in making flexible foams, it 15 is available from the Dow Chemical Co.

PAPI 27 is a 2.7 functional polymeric MDI (methylenediisocyanate) with an equivalent weight of 134. Used in making rigid foams and available from the Dow Chemical Co.

20 Firemaster-550 is a mixture of halogenated aryl esters and aromatic phosphates. Used as a flame retardant in flexible foams. Available from Great Lakes Chemical Co.

L6900 is a silicone surfactant used in rigid foams. Available from Crompton Osi Specialties Co.

25 HCFC Forane 141b is a hydrochlorofluorocarbon blowing agent used in rigid foams. Available from Atonfina Chemicals, Inc.

Dypol 6862 is a solvent free pale yellow branched poly alcohol with ester and ether groups, available from Dyflex.

5 Baylith L is a 50% mixture of 3 angstrom molecular sieves in Castor oil, available from Bayer.

VORANATE M 220 is a polymeric MDI functionality 2.7 available from The Dow Chemical Company.

ISONATE M 143 is a carbodiimide modified pure MDI available from The Dow Chemical Company.

10

General Procedure for the Production of Polyurethanes from Vegetable Oil-Based (VOB) Polyols

All of the polyol components of a given formulation except the tin catalyst (stannous octanoate in dioctylphthalate, 15 T-95), were individually metered and weighed into a one quart capacity metal cup. The contents were premixed for 15 seconds at 1800 rpm using a pin type mixer. The tin catalyst, dispensed by volume, was then added to the stirred components and mixed for an additional 15 seconds 20 at 1800 rpm. A stoichiometric amount of Toluene Diisocyanate (Voranate T-80), was then added to the cup and vigorously mixed for 3 seconds at 2400 rpm. The cup contents were then poured into a 15"x 15"x 10" wooden box lined with a polyethylene bag. The blowoff time and any 25 other distinct reaction characteristics were recorded. The foam buns were allowed to cure overnight under a ventilated fume hood. They were then placed in ambient storage and submitted for physical property assessment using ASTM test method designation D 3574-95.

Where indicated, other slabstock foam data were generated on conventional continuous machines (Polymech or UBT) featuring a reciprocating mixing head and high pressure injection of all streams except the polyol. The polyol and isocyanate temperatures were maintained at around 23°C. The polyol output was 20 kg/min. (The polyols used in Examples 34-36 and Examples 49-51 were blended with Voranol 3137A either in the polyol tank or in the mixing head.).

5

10 According to the general procedure, the foams were prepared according to the following formulations, with the results of mechanical testing included in the tables:

Table VIII: Examples 31-33. Box foams prepared from hydroxymethyl stearate polyols

Example #	31	32	33
<b>Components</b>			
V-3137A	80	65	50
Polyol of Example # 6	20	35	50
Water	4.5	4.5	4.5
D-8264	0.12	0.12	0.12
DC5160	1	1	1
T-95, mils	0.4	0.4	0.4
Index	110	110	110
TDI	57.8	58.2	58.5
<b>Properties</b>			
Blow-Off	96	95	94
Air Flow	4.2	4.3	3.3
Com. Set.	3.7	4.3	4.4
Density	1.44	1.54	1.51
25% IFD	39.8	41.3	43.2
65% IFD	71.6	76.8	82.1
Guide Factor	27.6	26.8	28.6
Resiliency	38	37	36
Tensile	12.7	12.5	12.1
Tear	1.7	1.7	1.6
Elongation	104	90	74

Table IX: Examples 34-36. Flexible slabstock foam produced from hydroxymethyl stearate polyols on a continuous foam machine:

Example #	34	35	36
<b>Components</b>			
Voranol* 3137A	80	65	50
Combined Polyols of Examples # 19 and #20	20	35	50
Water	4.5	4.5	4.5
D - 8264	0.12	0.12	0.12
DC - 5160	1.0	1.0	1.0
DABCO T9	0.2	0.2	0.2
Voranate T-80	57.8	58.1	58.4
<b>Foam Properties</b>			
Density (kg/m <sup>3</sup> )	21.1	21.2	21.4
CFD 40% (kPa)	3.9	4.3	4.5
IFD 40%	156.2	168.4	175.9
SAG Factor	2.7	2.8	2.9
Hysterisis (%)	45	49	53
Resilience (%)	40	36	36
Guide Factor	7.4	7.9	8.2
Airflow (cfm)	3.1	2.4	2.1
Tensile (kPa)	89	80	78
Elongation (%)	142	128	102
Tear (N/m)	426	337	309

5 These Examples were produced on a continuous slabstock foam production machine at a TDI index of 110.

Table X: Examples 37-41. Flexible molded foam produced from hydroxymethyl stearate polyols

Example #		37	38	39	40	41
<b>Components</b>						
Specflex NC-632		70.00	60.00	50.00	70.00	70.00
Specflex NC-700		20.00	20.00	20.00	20.00	20.00
Combined Polyols of Examples #19 and #20		10.00	20.00	30.00	10.00	10.00
Voranol* CP 1421					1.00	
Polycat 58						0.30
Niax A-300		0.25	0.25	0.25	0.25	0.25
Niax A-400		0.10	0.10	0.10	0.10	0.10
Tegostab-b8708		0.80	0.80	0.80	0.80	0.80
Dabco 33LV		0.30	0.30	0.30	0.30	0.30
Dabco DC 5164		0.20	0.20	0.20	0.20	0.20
DEOA PURE		1.00	1.00	1.00	1.00	1.00
WATER		3.70	3.70	3.70	3.70	3.70
<b>TOTAL PARTS</b>		<b>106.35</b>	<b>106.35</b>	<b>106.35</b>	<b>107.35</b>	<b>106.65</b>
<b>WATER CONTENT OF THE BLEND</b>		<b>3.65</b>	<b>3.65</b>	<b>3.65</b>	<b>3.61</b>	<b>3.64</b>
<b>OH# OF THE POLYOL BLEND</b>		<b>56.91</b>	<b>60.24</b>	<b>63.58</b>	<b>56.60</b>	<b>59.72</b>
<b>INDEX</b>		100	100	100	100	100
<b>Foam Properties</b>						
Density Core		32.1	32.8	33.2	33.5	33.0
CFD 50%		4.9	5.5	5.6	5.0	4.7
Tensile Strength		106	114	125	109	102
Elongation		104	101	106	105	100
Tear Strength		281	271	284	255	266
Resilience		58	57	55	57	61
Air Flow		1.61	2.49	1.68	2.28	2.62
Compression Set 50%		6.5	6.4	8.1	6.0	6.2
Compression Set 90%		11.3	11.3	13.5	8.7	9.7
Wet Compression set 70%		21.3	20.7	24.3	17.0	22.1

**Table XI:** Examples 42-44. Flexible foam produced from seed oil polyol as a 35% and 50% (w/w) blend with conventional EO/PO polyol.

Example #	42	43	44
<b>Components</b>			
V-3137a	65	50	65
Polyol of Example # 12	35	50	
Polyol of Example # 13			35
Water	4.5	4.5	4.5
DC-5160	1	1	1
D-8264	0.12	0.12	0.12
T-95	0.4	0.5	0.7
Index	110	110	110
TDI	58.4	58.9	57.7
Blowoff	126	105	95
Airflow (cfm)	4.3	2.5	2.6
Density (pcf)	1.48	1.41	1.4
Tear (pli)	1.4	1	1.3
Mean(psi)	12.2	13.3	12.8
%Elongation	69.5	67.8	83.7
CS_90orig	4.2	4.9	4.3
IFD_Slab:			
25% lbs.	39.2	47.2	44.9
65% lbs.	76.3	92.2	84.3
Resiliency	30	33	33
GuideFactor	26.5	33.5	32.1

Table XIII: Example 45: Flexible foam produced from seed oil polyol as a 65% (w/w) blend with conventional EO/PO polyol

Example #	
	45
V-3136	35
Polyol of Example #15	65
Water	4.5
D-8264	0.12
L-626	1
DC5160	1
T-95, mils	0.32
Index	110
TDI	59.4
Blow-Off (sec)	88
Air Flow	Not determined
Com. Set.	Not determined
Density	Not determined
25% IFD	Not determined
65% IFD	Not determined
Guide Factor	Not determined
Resiliency	Not determined
Tensile	Not determined
Tear	Not determined

5

10

Table XIII: Examples 46-48: Flexible foams produced from seed oil polyol as 100% of the polyol component, and at different isocyanate indices

Example #	46	47	48
V-3137A			
Polyol of Example # 15	100	100	100
Water	4.5	4.5	4.5
D-8264	0.12	0.12	0.12
L-626	3	3	3
DC5160			
T-95, mils	0.38	0.28	0.38
Index	100	110	120
TD	57.4	63.1	68.8
Blow-Off		87	104
Air Flow	0.91	0.63	0.31
Density	1.56	1.52	1.48
25% IFD	39.6	37.8	49.6
65% IFD	87.9	93.6	95.5
Guide Factor	25.4	24.9	33.5
Resiliency	28	29	32

**Table XIV: Examples 49-51: Continuous Production of flexible slabstock foam from vegetable oil based polyol at 20%, 35% and 50%**

Example #	49	50	51
<b>Components</b>			
V-3137	80	65	50
Combined Polyol of Examples # 21 and #22	20	35	50
Water	4.5	4.5	4.5
D-8264	0.12	0.12	0.12
DC5160	1	1	1
DABCO T-9	0.16	0.14	0.12
Index	110	110	110
Voranate T80	57.4	58.4	58.8
<b>Properties</b>			
Air Flow	4.5	4.1	4.1
Compression Set 75%	3.5	4.7	7.8
Density (kg/m <sup>3</sup> )	22.8	23.4	22.5
40% IFD	166.6	167.5	186.4
Guide Factor	7.3	7.2	8.3
SAG	2.7	2.7	2.9
Resiliency (%)	42	39	39
Tensile (kPa)	60	61	75
Tear (N/m)	279	266	194
Elongation	88	93	71

Table XV: Example 52: Flexible foam produced from seed oil polyol with copolymer polyol

<b>Example #</b>	52
<b>Components</b>	
Voranol-3136	15
Voranol-3943A	35
Polyol of Example # 15	50
Water	
D-8264	0.12
DC5160	1
T-95, mils	0.32
Index	110
TDI	57.5
Blow-Off (sec)	93
Air Flow	4
Com. Set.	1.9
Density	1.48
25% IFD	37.61
65% IFD	92.3
Guide Factor	25.4
Resiliency	31

Table XVI: Examples 53-56: Flexible molded foams produced from seed oil polyol with copolymer polyol:

Example #		53	54	55	56
<b>Components</b>					
Specflex NC-632		70.00	60.00	50.00	40.00
Specflex NC-700		20.00	20.00	20.00	20.00
Combined Polyols from Examples #21 and #22		10.00	20.00	30.00	40.00
Voranol CP 1421					
Polycat 58					
Niax A-300		0.25	0.25	0.25	0.25
Niax A-400		0.10	0.10	0.10	0.10
Tegostab-b8708		0.80	0.80	0.80	0.80
Dabco 33LV		0.30	0.30	0.30	0.30
Dabco DC 5164		0.20	0.20	0.20	0.20
DEOA PURE		1.00	1.00	1.00	1.00
WATER		3.70	3.70	3.70	3.70
<b>TOTAL PARTS</b>		<b>106.35</b>	<b>106.35</b>	<b>106.35</b>	<b>106.35</b>
<b>WATER CONTENT OF THE BLEND</b>		<b>3.65</b>	<b>3.65</b>	<b>3.65</b>	<b>3.65</b>
<b>OH# OF THE POLYOL BLEND</b>		<b>57.71</b>	<b>61.84</b>	<b>65.98</b>	<b>70.12</b>
<b>INDEX</b>		<b>100</b>	<b>100</b>	<b>100</b>	<b>100</b>

Density Core		35.4	36.8	35.5	33.8
CFD 50%		5.6	6.6	6.2	6.4
Tensile Strength		107	134	109	107
Elongation		103	107	93	84
Tear Strength		223	220	237	198
Resilience		53.5	52	48.5	43.5
Air Flow		1.0	1.7	1.5	1.3
Hardness Loss after Fatigue		32	34	37	40
Compression Set	50%	7	8	10	12
Compression Set	90%	9	10	14	17
Wet Compression set	70%	17	20	22	24

Example 57: Flexible foam produced from seed oil polyol using high water level in the formulation

Table XVII: Example 57 Components and Characteristics.

Example #	
	57
V-3137A	50
Polyol of Example #16	50
Water	6
D-8264	0.1
DC5160	1
T-95, mils	0.35
Index	110
TDI	75.1
Blow-Off	107
Air Flow	4.3
Density	1.15
25% IFD	33.5
65% IFD	78.8
Guide Factor	29.1
Resiliency	34

5 Examples 58-62. Rigid Foams prepared from seed oil polyols

General Procedure for the production of rigid foams:

Foam components were measured to an appropriate total blended mass which was appropriate for the size of the  
 10 container into which the foam will be formed, according to the ratios in the Table XVIII for Examples 58-62. The isocyanate component was weighed into a mixing cup separately. All components except for the isocyanate were combined in a mixing cup and stirred at 1000 rpm for 6  
 15 seconds. The isocyanate was then added to the blend of

all other components in the polyol, and this new mixture was blended at 1000 rpm for 6 seconds. The foam mixture was then poured into the container in which the foam was to be formed. The following characteristics were measured:

5 gel-time which is defined as when a tongue depressor inserted into the foam draws strings when removed (not surface stringing but stringing from foam Interior), and tack free-time which is defined as when the foam surface is no longer tacky, or does not adhere to touch. Results  
 10 of these Examples are shown in Table XVIII

Table XVIII: Results of Examples 58-62

<u>Example #</u>	<b>58</b>	<b>59</b>	<b>60</b>	<b>61</b>	<b>62</b>
<b><u>Components</u></b>					
Voranol 360	50	75	50	25	0
Polyol of Example # 25	50				
Polyol of Example # 27		25	50	75	100
Polycat 5	1	1	1	1	1
Polycat 8	2	2	2	2	2
Polycat 46	1	1	1	1	1
L-6900	2.15	2.15	2.15	2.15	2.15
Water	2.58	2.58	2.58	2.58	2.58
HCFC-141b	20	20	20	20	20
PAPI 27	137	137	137	137	137
<b><u>Properties</u></b>					
Gel Time (sec)	29	35	41	40	30
Tack Free (sec)	40	63	66	65	45
Crown Density (lbs/cft)	1.59	1.41	1.38	1.499	1.446

Examples 63 and 64: Elastomers and coatings prepared from vegetable oil-based polyol

15 Polyols of the examples were blended together by adding molecular sieves (Baylith L) and mixing by hand for 5 minutes. The blend is then degassed in a vacuum oven until no bubbles were retained.

Method for production of an elastomer plate or a coating

The polyol of the example and the isocyanate were mixed at room temperature for a minimum of 1 minute to achieve complete homogeneity. The resulting mixture was cast into 5 a mold of 2mm thickness for preparation of an elastomer, or cast onto a flat surface for the preparation of a coating. Curing of a thin layer (2mm) at atmospheric condition gave a good elastomer without bubbles. Alternatively, the casting was cured in an oven for 1 hour 10 at 75°C.

The resulting polyurethane sample was kept at room temperature for 7 days before testing, or alternatively was post cured at 75°C 10 hours before testing.

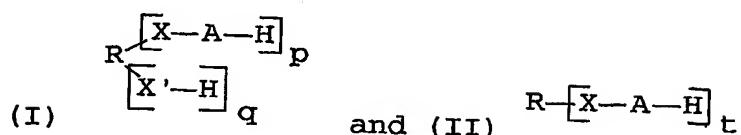
Table XIX: Examples 62 and 63 Components and Results.

Example #		62	63
<b>Components</b>			
Castor oil			
Dypol 6862			
Polyol of Example #18		100	100
Baylith L		5	5
VORANATE M 220		42.5	
ISONATE M 143			45.5
<b>Properties</b>			
Tensile strength	MPa	4.7	4.0
Elongation	%	56	76
Tear strength	N/cm	56	56
Pot life ( geltimer)	min	48	55
Shore A (7days)		70	73
Shore D (7 days)		24	20

15

WHAT IS CLAIMED IS:

1. A vegetable oil based polyol comprised of

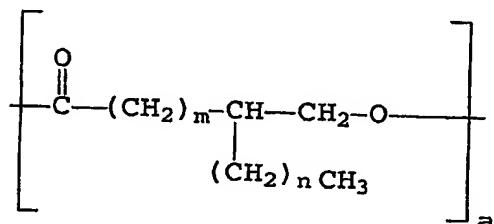


5 where

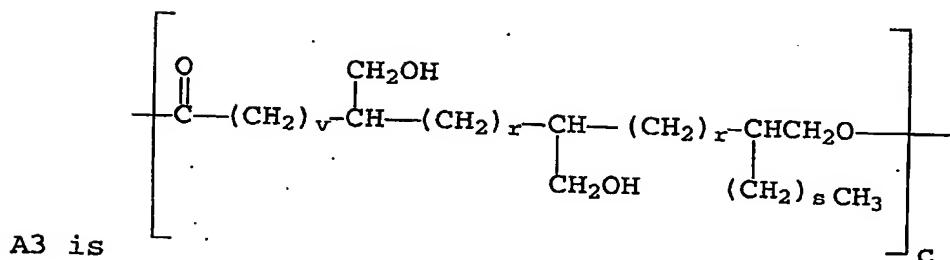
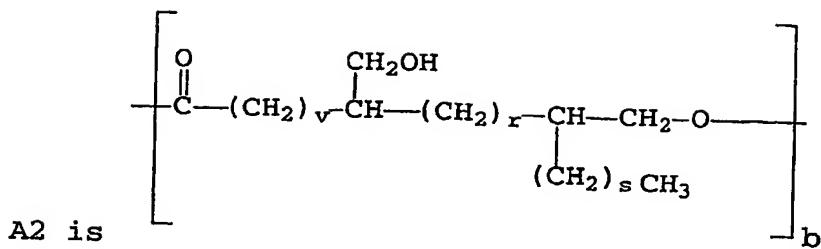
R is a residue of a polyol, polyamine or aminoalcohol initiator;

X and X' may the same or different and is O, N or NH;  
 p is an integer from 1 to 5; q is an integer from 1 to 5  
 10 wherein p + q is from 3 to 8, t is an integer from 3 to 8  
 and A may be the same or different and is selected from  
 the group consisting of A1, A2 and A3 where

A1 is



15



where m, n, v, r, s, a, b and c are integers and m is  
 5 greater than 3, n greater than or equal to zero and m+n is  
 from 11 to 19, v is greater than 3, r is greater than or  
 equal to zero, s is greater than or equal to zero and  
 v+r+s is from 10 to 18, a is from 0 to 35, b is from 0 to  
 10 35 and c is from 0 to 35, so long as that all a's, b's and  
 c's in any molecule of the vegetable oil based polyol are  
 not all zero and  $(a+b+c)/(p+q+t)$  is about 5 to about 100  
 in the vegetable oil based polyol.

2. The vegetable oil based polyol of Claim 1  
 wherein at least a portion of A is A3.

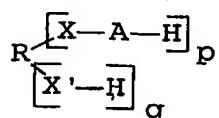
15 3. The vegetable oil based polyol of Claim 2  
 wherein the amount of A3 present in the vegetable oil  
 based polyol is at least about 0.01% to 25% by weight of  
 the vegetable oil based polyol.

4. The vegetable oil based polyol of Claim 1  
 20 wherein the initiator is of a polyol, polyamine or

aminoalcohol that has a primary hydroxyl or primary amine and a secondary hydroxyl or secondary amine group.

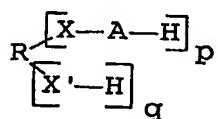
5. The vegetable oil based polyol of Claim 4 wherein the initiator has a secondary hydroxyl group.

5 6. The vegetable oil based polyol of Claim 4 wherein at least a portion of the vegetable oil based polyol has a structure



10 where at least one X'-H group is a primary hydroxyl or primary amine and at least one X-A-H is located at a position corresponding to a secondary hydroxyl or secondary amine of the initiator.

15 7. The vegetable oil based polyol of Claim 6 wherein at least a portion of the vegetable oil based polyol has a structure:



20 where all of the X'-H groups are a primary hydroxyl or primary amine and all of the X-A-H groups are located at a position corresponding to a secondary hydroxyl or secondary amine of initiator.

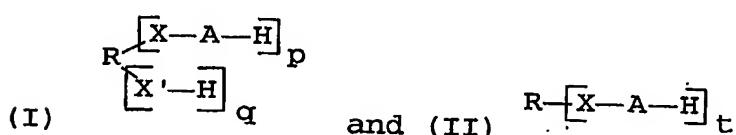
8. The vegetable oil based polyol of Claim 7 wherein the initiator is selected from the group consisting of trimethylolpropane; pentaerythritol; sorbitol; sucrose; glycerol; bis-3-aminopropyl 5 methylamine; diethylene triamine; 9(1)-hydroxymethyloctadecanol, 1,2,6-hexanetriol; any of the aforementioned where at least one of the alcohol or amine groups present therein has been reacted with ethylene oxide, propylene oxide or mixture thereof; and combination 10 thereof.

9. The vegetable oil based polyol of Claim 1 wherein the initiator is glycerol, pentaerythritol, sucrose, sorbitol, an ethoxylated glycerol, propoxylated glycerol, ethoxylated pentaerthritol, propoxylated 15 glycerol or mixture thereof.

10. The vegetable oil based polyol of Claim 1 wherein the initiator is glycerol or glycerol where at least one of the alcohol groups of the glycerol has been reacted with ethylene oxide or propylene oxide.

20 11. The vegetable oil based polyol of Claim 10 wherein the initiator is glycerol.

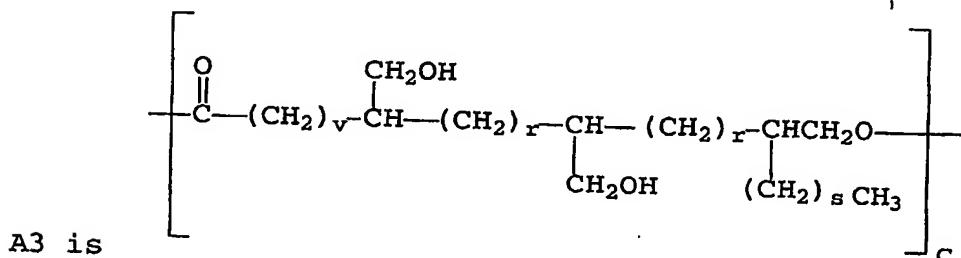
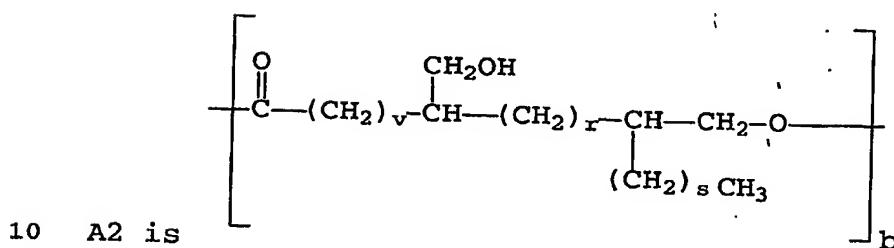
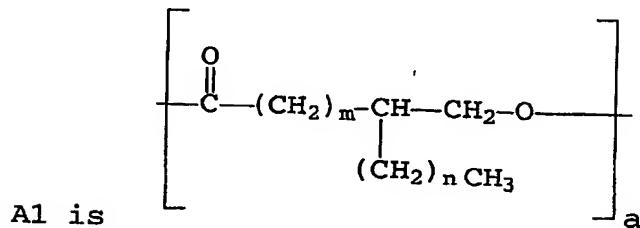
12. A vegetable oil based polyol comprised of



where

25 R is a residue of a polyol, polyamine or aminoalcohol initiator;

X and X' may the same or different and is O, N or NH;  
 p is an integer from 1 to 5; q is an integer from 1 to 5  
 wherein p + q is from 2 to 8, t is an integer from 2 to 8  
 and A may be the same or different and is selected from  
 5 the group consisting of A1, A2 and A3 where



where m, n, v, r, s, a, b and c are integers and m is  
 greater than 3, n greater than or equal to zero and m+n is  
 15 from 11 to 19, v is greater than 3, r is greater than or

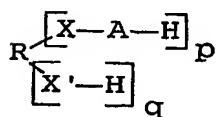
equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18, a is from 0 to 35, b is from 0 to 35 and c is from 0 to 35, so long as that all a's, b's and c's are essentially not all zero, at least a portion of A 5 is A3 and  $(a+b+c)/(p+q+t)$  is about 1 to about 100 in the vegetable oil based polyol.

13. The vegetable based oil of Claim 12 wherein the  $(a+b+c)/(p+q+t)$  is about 5 to 100.

14. The vegetable based oil of Claim 13 wherein 10 the  $(a+b+c)/(p+q+t)$  is about 7 to 100.

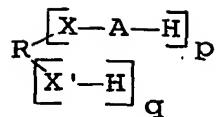
15. The vegetable based oil of Claim 12 wherein the initiator has a secondary hydroxyl group.

16. The vegetable oil based polyol of Claim 12 wherein at least a portion of the vegetable oil based 15 polyol has a structure



where at least one X'-H group is a primary hydroxyl or primary amine and at least one X-A-H is located at a 20 position corresponding to a secondary hydroxyl or secondary amine of the initiator.

17. The vegetable oil based polyol of Claim 16 wherein at least a portion of the vegetable oil based polyol has a structure:



where all of the X'-H groups are a primary hydroxyl or primary amine and all of the X-A-H groups are located at a position corresponding to a secondary hydroxyl or  
 5 secondary amine of the initiator.

18. The vegetable oil based polyol of Claim 17 wherein the initiator is glycerol.

19. The vegetable oil based polyol of Claim 11 wherein the initiator is selected from the group  
 10 consisting of neopentylglycol; 1,4-cyclohexane diol; 2,5-hexanediol; 1,6-hexanediol; 1,2-propylene glycol; trimethylolpropane; pentaerythritol; sorbitol; sucrose; glycerol; 1,6-hexanediol; 1,4-butanediol; ethylene glycol; diethylene glycol; triethylene glycol; bis-3-aminopropyl  
 15 methylamine; ethylene diamine; diethylene triamine; 9(1)-hydroxymethyloctadecanol; 1,4-bishydroxymethylcyclohexane; 8,8-bis(hydroxymethyl)tricyclo[5.2.1.0<sup>2,6</sup>]decene; Dimerol alcohol; hydrogenated bisphenol; 9,9(10,10)-bishydroxymethyloctadecanol; 1,2,6-hexanetriol; any of the  
 20 aforementioned where at least one of the alcohol or amine groups present therein has been reacted with ethylene oxide, propylene oxide or mixture thereof; and combination thereof.

20. The vegetable oil based polyol of Claim 19  
 25 wherein the initiator is glycerol or glycerol where at least one of the alcohol groups of the glycerol has been reacted with ethylene oxide or propylene oxide.

21. The vegetable oil based polyol of Claim 1 wherein vegetable based polyol is a liquid and has a weight average molecular weight of at least 350..

22. The vegetable oil based polyol of Claim 21  
5 wherein the weight average molecular weight is at least about 1500.

23. The vegetable oil based polyol of Claim 22 wherein the weight average molecular weight is at least about 1800.

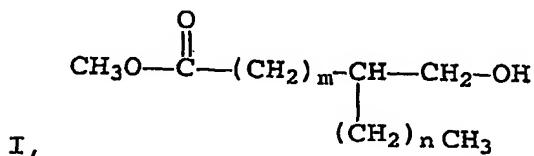
10 24. The vegetable oil based polyol of Claim 12 wherein vegetable based polyol is a liquid and has an average molecular weight of at least about 350 by weight.

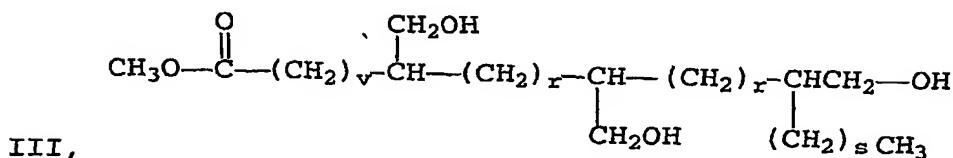
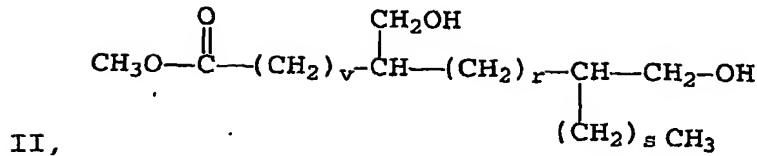
25. The vegetable oil based polyol of Claim 24  
wherein the average molecular weight is at least about  
15 1500 by weight.

26. The vegetable oil based polyol of Claim 25  
wherein the weight average molecular weight is at least about 1800.

27. A process to make a vegetable based polyol,  
20 the process comprising,

i) mixing an initiator that is a polyol, polyamine, aminoalcohol or mixture thereof, and a vegetable oil based monomer having at least one of the formulae:





where m, n, v, r, and s are integers and m is greater than 3, n greater than or equal to zero and m+n is from 11 to 19, v is greater than 3, r is greater than or equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18, and

ii) heating the mixture to a reaction temperature, for a reaction time, while under a vacuum and in the presence of an amount of a catalyst sufficient to form the vegetable based polyol.

28. The process of Claim 27 wherein the catalyst is a tin catalyst and the amount of catalyst is at least about 100 parts per million by weight of the total mixture.

29. The process of Claim 28 wherein the amount of catalyst is at least about 250 parts per million.

30. The process of Claim 27 wherein the catalyst is titanium catalyst and the amount of catalyst is at least about 100 parts per million by weight.

31. The process of Claim 30 wherein the amount of catalyst is at least about 500 parts per million.

32. The process of Claim 28 wherein the catalyst is selected from the group consisting of tin (II) ethylheptanoate, tin (II) octanoate, dibutyltin (IV) dilaurate and combination thereof.

5 33. The process of Claim 30 wherein the catalyst is titanium tetraisopropoxide, titanium tetraisobutoxide or combination thereof

34. The method of Claim 27 wherein the catalyst is an enzyme catalyst.

10 35. The method of Claim 34 wherein the catalyst is lipase.

36. The method of Claim 27 wherein the catalyst is comprised of a carbonate catalyst.

15 37. The method of Claim 36 wherein the carbonate catalyst is  $K_2CO_3$ ,  $NaHCO_3$  or combination thereof.

38. The process of Claim 27 wherein the initiator has at least one secondary hydroxyl or secondary aminogroup.

20 39. The process of Claim 27 wherein the initiator is glycerol.

40. The process of Claim 27, wherein the initiator has volatility such that at the reaction temperature and vacuum the initiator would be in the absence of the vegetable oil based monomer substantially evaporated in at most about 120 minutes.

41. A polyurethane comprised of the reaction product of a polyisocyanate and the vegetable based polyol of Claim 1.

42. The polyurethane of Claim 41 wherein the polyurethane is a flexible foam.

43. The polyurethane of Claim 42 wherein the polyurethane foam is the reaction product of a 5 polyisocyanate and the vegetable based polyol wherein the polyurethane is formed in the absence of any other polyol.

44. A polyurethane comprised of the reaction product of a polyisocyanate and the vegetable based polyol of Claim 12.

10 45. The polyurethane of Claim 44 wherein the polyurethane is a flexible foam.

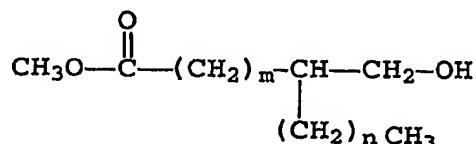
46. The polyurethane of Claim 44 wherein the polyurethane foam is the reaction product of a 15 polyisocyanate and the vegetable based polyol wherein the polyurethane is formed in the absence of any other polyol.

47. The polyurethane of Claim 41 wherein the foam has an alkoxy silane surfactant.

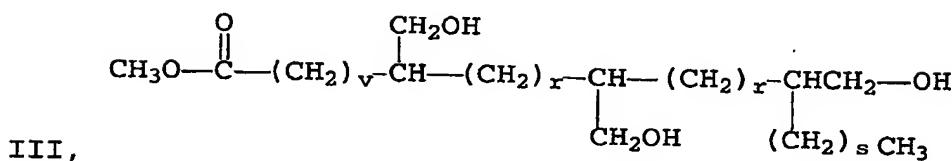
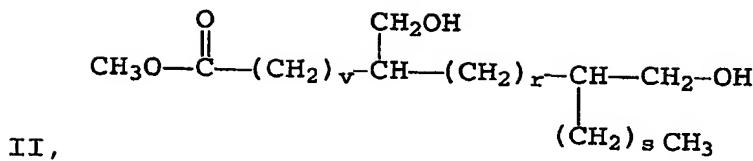
48. The polyurethane of Claim 44 wherein the foam has an alkoxy silane surfactant.

20 49. A process to make a vegetable based polyol, the process comprising,

i) heating, in the presence of a catalyst a vegetable oil based monomer having at least one of the formulae:



25 I,



5 where m, n, v, r, and s are integers and m is greater than 3, n greater than or equal to zero and m+n is from 11 to 19, v is greater than 3, r is greater than or equal to zero, s is greater than or equal to zero and v+r+s is from 10 to 18 until some portion of the  
10 VOB monomers have reacted and subsequently

15 ii) introducing an initiator that is a polyol, polyamine, aminoalcohol or mixture thereof to the reacted VOB monomers of step (i) for a time and temperature sufficient to form the vegetable based polyol under vacuum.

50. The process of Claim 49 wherein the initiator is volatile at the reaction conditions of step (ii)

ABSTRACT OF THE DISCLOSURE

Polyols useful in the manufacture of polyurethanes are disclosed. The polyols are prepared by reacting a vegetable oil based (hydroxymethyl containing) monomer with a polyol, polyamine or aminoalcohol under vacuum.

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